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OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT INITIATION

Date: August 15, 1973

Project Title: Porous Composites for Fiber Tip Pens

Project No: E-27-619

Principal Investigator Dr. Wayne C. Tincher

Sponsor: Scripto, Inc.

Agreement Period: From 8/1/73 Until 10/31/73 (approximately)

Type Agreement: Standard Industrial dated 7/2/73

Amount: $6,955

Reports Required: Monthly Progress Letters; Final Report

Sponsor Contact Person (s):

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Assigned to: School of Textile Engineering

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RA-3 (6-71)

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GEORGIA INSTITUTE OF TECHNOLOGY

OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT TERMINATION

Date: April 2, 1975

Project Title: Porous Composites for Fiber Tip Pens

Project No: E-27-619

Principal Investigator: Dr. Wayne C. Tincher

Sponsor: Scripto, Inc.

Effective Termination Date: 10/31/74

Clearance of Accounting Charges: 10/31/74

Grant/Contract Closeout Actions Remaining:

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RA-4 (5/70)

E-27-619

Georgia Institute of Technology
School of Textile Engineering
Atlanta, Georgia 30332

June 1, 1974

MEMORANDUM

To: Mr. E. P. Cofield, Jr.
Scripto Incorporated

From: Dr. W. C. Tincher
Associate Professor

Subject: Monthly Progress Letter - Project E-27-619
"Porous Composites for Fiber Tip Pens"

Preliminary experiments have shown that it is possible to bond nylon 66 filaments in a pen tip using low-melting nylon 6 fiber as the bonding agent. Several samples have been produced by winding 50 to 60 ends of a textured 143 denier nylon 66 yarn (melting point 252-254°C) and various quantities of a 70 denier nylon 6 yarn (melting point 215-218°C) in a mold and heating in an oven at 240°C for 30 minutes. Microscopic examination of the samples revealed many small beads of molten polymer in the pen tips.

Best properties have been obtained with a 50/50 ratio of nylon 66 to nylon 6. The thermally bonded tip would readily transport ink from a filler tube but did not have the abrasion resistance necessary for pen tips. The principal difficulty appears to be a result of thermal degradation of the nylon 6 component due to the long heating cycle required in a static molding operation.

Equipment is now being constructed which will allow treatment of a yarn bundle at 220-240°C in a preheated die. This will permit much shorter residence times above the nylon 6 melting point and should give stronger interfiber bonds.

File: E-27-619

Georgia Institute of Technology
School of Textile Engineering
Atlanta, Georgia 30332

July 3, 1974

To: Mr. E. P. Cofield, Jr.
Scripto Incorporated

From: Dr. W. C. Tincher
Associate Professor

Subject: Monthly Progress Letter - Project E-27-619
"Porous Composites for Fiber Tip Pens"

The "bench-top" unit for preparation of rod stock samples by the melt bonding method has been set up. Up to 18 inch lengths of rod stock can be made with this unit. Initial runs have produced samples with significantly better properties than those obtained by the static molding technique used previously.

Best properties to date have been obtained with a twisted yarn containing 2 ends of a 70 denier nylon 6 and 1 end of a 143 denier nylon 6,6. Forty-four ends of this yarn were passed through the heated die at 220°C with a residence time of approximately 1 minute. A short sample of this rod stock is attached to this report. Although this sample probably does not have properties sufficient for pen top fabrication, it does demonstrate the feasibility of the thermal bonding technique.

During the next month a number of samples will be prepared to study the effect of yarn geometry, nylon 6 content, and nylon 6 filament size on melt bonded rod stock.

WCT/ ed

Our 75th Year

1899-1974

File: E-27-619

GEORGIA INSTITUTE OF TECHNOLOGY
SCHOOL OF TEXTILE ENGINEERING
ATLANTA, GEORGIA 30332

August 5, 1974

To: Mr. E. P. Cofield, Jr.
Scripto Incorporated

From: Dr. W. C. Tincher
Associate Professor

Subject: Monthly Progress Letter - Project E-27-619
"Porous Composites for Fiber Tip Pens"

A systematic study of the effect of process variables on the characteristics of melt bonded pen tips is underway. The effects of nylon 6 content, nylon 6,6 content, and yarn geometry are under study. The initial series of samples has been prepared using untwisted yarns to produce the rod stock. These samples are listed in Table 1.

Preliminary examination of the samples shows clear differences in physical properties and in ink transport capabilities. Increasing the nylon 6 to nylon 6,6 ratio greatly reduces the rate of ink transport and increases the "hardness" of the tip. The number of nylon 6,6 yarns in the bundle also significantly alters the properties. Measurements of ink rise by capillarity show that sample 110-001-1 with 56 nylon 6,6 yarns has a rise rate of approximately 0.5 inches per minute whereas sample 110-001-2 with 60 nylon 6,6 yarns has an ink rise rate only 1/2 as fast (0.25 inches per minute). Further characterization of these samples should give estimates of the limits within which the process can produce reasonable rod stock.

Some experiments comparing rod stock produced from twisted and untwisted yarns suggest that yarn geometry may be an important factor in pen tip properties. This parameter will be further investigated in the coming month.

TABLE 1

Sample Number	No. of Yarns Nylon 6,6 143/71	No. of Yarns Nylon 6 70/32	Nylon 6 to Nylon 6,6 Ratio	Twist	Speed (In/min)	Temp. °C
110-001-1	56	56	1:2	0	1	218-237
110-001-2	60	60	1:2	0	1	218-237
110-002-1	50	100	1:1	0	1	218-237
110-002-2	56	112	1:1	0	1	218-237
110-002-3	60	40	1:3	0	1	218-237
110-002-4	54	36	1:3	0	1	218-237
110-002-5	48	32	1:3	0	1	218-237

E-27-619

GEORGIA INSTITUTE OF TECHNOLOGY
SCHOOL OF TEXTILE ENGINEERING
ATLANTA, GEORGIA 30332

August 29, 1973

MEMORANDUM

To: Mr. E. P. Cofield, Jr.
Scripto Incorporated

From: Dr. W. C. Tincher
Associate Professor

Subject: Monthly Progress Letter - Project E-27-619
"Porous Composites for Fiber Tip Pens"

Major effort during the initial phase of this project has been directed toward assembly of the necessary equipment and supplies for preparation of hollow filament composites and development of procedures for pen tip evaluation.

Several samples of hollow filament yarns have been obtained from fiber manufacturers for construction of hollow filament composite pen tips. Microscopic examination of these fibers confirmed that they have continuous channels parallel with the fiber axis. Both single channel and multiple channel filaments have been obtained for study.

Composite pen tip fabrication equipment has been set up to permit preparation of pen tip rod stock approximately 0.08" in diameter. This equipment consists of a tension control device (hysteresis brake), resin application equipment, and a mold for formation and curing of the fiber composites. The tension, resin pick-up and fiber loading can be varied independently. Initial composite specimens are now being fabricated.

Procedures for preliminary evaluation of composite pen tips have also been studied. Capillary rise rates of ink samples in a number of commercial pen tips have been studied and techniques have been developed to permit preliminary evaluation of pen tip candidates.

A number of hollow filament composites will be prepared and evaluated in the remainder of August and in early September.

WCT/cdb

File: E-27-619

Georgia Institute of Technology
School of Textile Engineering
Atlanta, Georgia 30332

September 6, 1974

TO : Mr. E. P. Cofield, Jr.
Scripto Incorporated

FROM : Dr. W. C. Tincher
Associate Professor

SUBJECT: Monthly Progress Letter - Project E-27-619
"Porous Composites for Fiber Tip Pens"

Seventeen samples of rod stock with various ratios of nylon 6 to nylon 6,6 both with and without prior twisting of the yarns have been prepared and evaluated this month. Details of the preparation of these samples are shown in Table 1.

Samples prepared this month and last month have been evaluated by observing rate of ink rise in the rod stock and by preparing crude pen tips from writing evaluation. Results of these preliminary evaluations are shown in Tables 2 and 3. Tips have been designated as "dry" if they would not transport sufficient ink for writing. Tips which produced a noticable weaker line after a period of continuous writing are designated "slightly dry." Other tips are listed as "good." In some cases the tips were obviously too weak for further consideration and have been so designated in Tables 2 and 3.

The results suggest two regions which may produce good tips. Tips with 50 to 55 ends of nylon 6,6 and a 6 to 6,6 ratio of 1:2 appear to have promising properties. Also samples with 55 to 60 ends of nylon 6,6 and a 6 to 6,6 ratio of 1:3 need further investigation. There appears to be little difference in samples produced from twisted and untwisted yarns. The untwisted yarns may show slightly better transport properties but the twisted yarns may give a tip with better physical properties. These differences will require evaluation on a writing machine.

Effort in September will be devoted to production of some samples for writing machine evaluation.

TABLE 1

Sample Number	No. of Yarns Nylon 6,6 143/71	No. of Yarns Nylon 6 70/32	Nylon 6 to Nylon 6,6 Ratio	Twist (Turns/In.)	Speed (In./Min.)	Temp. (oC)
110-002-6	50	50	1:2	0	1	218-237
110-003-1	50	50	1:2	~13 (1:1)	1	218-237
110-003-2	56	56	1:2	~13 (1:1)	1	218-237
110-003-3	60	60	1:2	~13 (1:1)	1	218-237
110-003-4	50	25	1:4	~13 (2:1)	1	218-237
110-003-5	80	40	1:4	~13 (2:1)	1	218-237
110-003-6	76	38	1:4	~13 (2:1)	1	218-237
110-003-7	60	30	1:4	~13 (2:1)	1	218-237
110-003-8	56	28	1:4	~13 (2:1)	1	218-237
110-004-1	69	46	1:3	~13 (3:2)	1	218-237
110-004-2	60	40	1:3	~13 (3:2)	1	218-237
110-004-3	54	36	1:3	~13 (3:2)	1	218-237
110-004-4	51	34	1:3	~13 (3:2)	1	218-237
110-005-1	66	44	1:3	~13 (3:2)	1	218-237
110-005-2	63	42	1:3	~13 (3:2)	1	218-237
110-005-3	57	38	1:3	~13 (3:2)	1	218-237
110-005-4	60	40	1:3	0	1	218-237

TABLE 2

Pen Tips Prepared From Untwisted Yarns

Ratio of Nylon 6 to Nylon 6,6

No. of Nylon 6,6 Yarns (143/71)	1:1	1:2	1:3
48			110-002-5 Weak
50	110-002-1 Dry	110-002-6 Good	
54			110-002-4 Good
56	110-002-2 Dry	110-001-1 Good	
60		110-001-2 Slightly Dry	110-002-3 110-005-4 Good

TABLE 3

Pen Tips Prepared from Twisted Yarns

Ratio of Nylon 6 to Nylon 6,6

	1:2	1:3	1:4
50 51	110-003-1 Slightly Dry	110-004-4	110-003-4
54		110-004-3 Good	
56 57	110-003-2 Dry	110-005-3 Good	110-003-8
60	110-003-3 Dry	110-004-2 Good	110-003-7 Good Weak
63		110-005-2 Dry	
66		110-005-1 Dry	
69		110-004-1 Dry	
76 80			110-003-5 110-003-6 Dry

E-27-619

GEORGIA INSTITUTE OF TECHNOLOGY

SCHOOL OF TEXTILE ENGINEERING

ATLANTA, GEORGIA 30332

October 1, 1973

MEMORANDUM

To: Mr. E. P. Cofield, Jr.
Scripto Incorporated

From: Dr. W. C. Tincher
Associate Professor

Subject: Monthly Progress Letter - Project E-27-619
"Porous Composites for Fiber Tip Pens"

Several samples of rod stock for hollow filament pen tips have been made and evaluated. All initial samples have been prepared using Dupont Antron II 1225-80 nylon yarn with four channels parallel with the fiber axis. This is a textured continuous filament yarn specifically designed for use in carpets. It was not possible to prepare tips with less than 11 strands or greater than 13 strands of this yarn. Specimens with 11 (total denier of 13,475), 12 (total denier of 14,700), and 13 strands (total denier of 15,925) were prepared for initial screening. Approximately 30% by weight of resin was added and samples were cured at 500°F for 2 minutes. Times for ink to rise 3/4" in each tip are given in Table 1 with similar data for 3 other types of pen tips selected for comparison. Microscopic examination of the tips indicated that ink carrying channels are present both within filaments and between filaments in the tips. Specimens of each of these tips are available for writing machine evaluation.

Rod stock prepared from two other types of hollow filament yarns are now being fabricated for testing. Samples with higher resin contents are also being prepared.

WCT/cdb

TABLE 1

TIME FOR INK TO RISE 3/4" IN PEN TIPS

	RED INK #3806B (SEC.)	BLACK INK #3886 (SEC.)
DOREX III	24.5	17.0
ANJA (REGULAR)	38.3	>100
ANJA (A.V.)	34.6	>100
11 STRANDS ANTRON II	12.8	21.4*
12 STRANDS ANTRON II	54.5	23.7*
13 STRANDS ANTRON II	69.5	26.2*

*The black ink was transported almost exclusively by the interior portion of the rod stock rendering observation of ink rise very difficult.

E-27-619

GEORGIA INSTITUTE OF TECHNOLOGY
SCHOOL OF TEXTILE ENGINEERING
ATLANTA, GEORGIA 30332
October 15, 1974

To: Mr. E. P. Cofield, Jr.
Scripto Incorporated

From: Dr. W. C. Tincher
Associate Professor

Subject: Monthly Progress Letter - Project E-27-619
"Porous Composites for Fiber Tip Pens"

Four samples of pen tip rod stock were prepared this month for writing instrument evaluation. These samples are listed below:

Sample Number	No. of Yarns Nylon 6,6	No. of Yarns Nylon 6	Ratio Nylon 6 to Nylon 6,6
110-004-002	60	40	1:3
017-075-003	54	36	1:3
017-075-004	54	54	1:2
017-075-001	50	50	1:2

All samples were prepared from twisted yarns. Writing machine evaluation of these samples should indicate the relative performance of samples with high and low levels of the fusible component (nylon 6) and with different quantities of Nylon 6,6 yarn. These samples were given to you on September 24.

Results of the writing machine evaluation will be needed for directing future work on the project.

tgx

E-27-619

Porous Composites for Fiber Tip Pens

Final Report
Project E-27-619

for

Scripto, Inc.

March 8, 1974

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

SUMMARY

This project was undertaken to evaluate possible modifications to the Scripto process for manufacture of fiber tip pens to improve control of pen quality. Acceptable pens must combine resistance to tip breakdown with sufficiently high porosity to deliver the quantity of ink necessary for writing.

Emphasis in the initial phases of the study was directed to evaluation of hollow fibers as a means for incorporating controlled porosity with acceptable mechanical properties. Three types of hollow filaments were evaluated, but none were capable of delivering the quantity of ink necessary for good writing performance.

During the course of these studies, it became apparent that the resin system employed in the Scripto process is the component creating greatest variation in pen tip quality. The evaporation of a large volume of solvent (95% of the resin system) at a controlled rate and to a precise residual level is extremely difficult to achieve in both laboratory and commercial processes. Development of a new fiber bonding system appears essential to establishing a controlled manufacturing process for fiber pen tips. Further research should be directed toward development of an improved bonding system.

TABLE OF CONTENTS

I. Introduction

Porous tip pens have captured a significant part of the writing instrument market in the past several years. Two principal approaches have been taken in manufacture of tips for these pens. One process involves use of either adhesive or thermal bonding to bind a bundle or mat of fibers in such a way that channels for ink flow are present between filaments. In the second process, spheres of a suitable plastic material are fused together by heat and pressure to form a porous pen tip. There are advantages and disadvantages to both of these approaches.

Scripto, Inc. has previously produced fiber pen tips by dipping a textured Nylon 6,6 fiber in a resin system and curing the resin to give controlled cementing of the filaments so that a porous pen tip is produced. This pen tip has excellent properties but significant difficulties were encountered in controlling the process to consistently yield high quality pen tips.

II. Objective

The objective of the present study was to evaluate possible modifications of the present process to improve control of pen quality. Primary emphasis in the present program has been directed to changes in the fiber component with some preliminary experiments on the resin system.

III. Conclusions

Pen tips were prepared with three types of hollow filament fibers in different resin systems. Tips were evaluated by measuring rate of rise of ink in tips, by intensive inspection under the microscope, and by preparing simple tips for writing experiments. These studies suggest that:

1. Hollow filaments do not provide significant advantages for improved control of pen tip quality.

2. The resin system employed for fiber bonding in the Scripto process is the component responsible for major problems in control of pen tip quality.

3. A bonding system with a more easily controlled cure cycle is essential for consistent production of high quality pen tips.

IV. Recommendations

Approximately one-third of the original budget for research on this project has been expended to date. It is recommended that the remaining funds be employed to develop a new bonding system for use in the Scripto fiber tip pen process. Two systems should be investigated -- a two-stage epoxy resin system and a thermal bonding system based on a mixture of low melting and high melting fibers. A thermal bonding system, in particular, has considerable promise as a novel, inexpensive, and easily controlled process for manufacture of fiber tip pens. Promising pen tip candidates should be evaluated in writing machine experiments.

Personnel at the Georgia Institute of Technology are familiar with the Scripto process for pen tip manufacture and have the necessary experience and facilities for development of an improved process for pen tip production.

V. Technical Details

A. Problem Definition

Scripto has produced pen tips from a multi-filament, Nylon 6,6 stretch yarn impregnated with a polyester resin and cured with an isocyanate. Yarns from a creel under controlled tension were dipped in a 5% solution of the adhesive in methyl ethyl ketone. Most of the solvent was removed by evaporation and the yarn passed into a heated die. The adhesive was partially cured in the die and the cure cycle completed in a post cure oven. Pen tips were then cut and shaped in a grinding operation.

Tips produced by this process had good properties but control of the process presented a number of problems. First, nylon stretch yarn undergoes significant changes in dimensions with only small changes in tension. It was necessary therefore to carefully control tension of the yarn during the process. Second, the various stages involved in a conversion of the liquid adhesive system to a solid polymer (i.e., evaporation of solvent, reaction of isocyanate groups, crosslinking) could not be independently controlled. These control problems manifest themselves either as tips with an excess of resin resulting in poor ink flow, or tips with a deficiency and/or improper distribution of resin resulting in poor mechanical properties. In the latter case, early destruction of the adhesion between filaments gives a splaying of the tip and a very wide writing line.

Several approaches were considered for possible solution to the problem of controlling pen quality.

1. Fibers with modified cross-sections

Fibers used in the present process have a round cross-sectional shape. Under tension and pressure cylindrical fibers can pack quite efficiently providing little space for ink flow between fibers. Nylon filaments with modified cross-sections such as star, trilobal, wedge, etc. are now commercially available and could provide better control of void space between filaments and thereby better control of ink flow. Some fiber tip pens are currently produced from non-round cross-section fibers.

2. Hollow Filaments

A number of fiber companies have recently developed hollow filaments to give special optical effects to textile products or for use in reverse osmosis units. The possibility was considered that these hollow fibers could serve as channels for ink flow. In this way the volume of ink flow would be independent of the resin content and the ink flow rate would not be influenced by factors noted above which influence tip quality.

3. Changes in the resin system

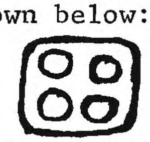
Since a number of difficulties in production control were related to application and curing of the resin matrix, a more easily controlled system could be developed to give the porous fiber composites needed for pen tips.

Of the possible approaches suggested above, Number 2 was selected for initial study. In addition to wide process control latitude, this approach might provide Scripto with a strong patent position and it could be pursued in the time and with the financial resources available for the study. Some preliminary work was also undertaken on modification of the resin system.

B. Experimental

1. Materials - Fiber

Three types of hollow fibers were selected for initial study. Primary studies were conducted on a Dupont Antron II textured nylon yarn. This fiber has the cross-section shown below:



Four channels run paralled with the fiber axis in each filament. It is designed for carpet applications and is available in a producer textured 80 filament, 1225 total denier yarn.

A round hollow filament cellulose acetate fiber with a large cross-section and a large single channel parallel with the fiber axis was employed in several tips. These fibers were approximately 0.2 mm in diameter with a 0.07 mm hole. This fiber was selected as an example of the larger filaments being developed for reverse osmosis applications.

The third fiber studied was a 50/50 blend of cellulose acetate and Nylon 4, approximately 0.05 mm in diameter with a round hole 0.02 mm in diameter parallel with the fiber axis. This fiber was representative of the smaller hollow filament fibers.

2. Materials - Resin

Initial studies were conducted using the resin system previously employed in manufacture of Scripto fiber pen tips. This resin system was supplied to Scripto by Industrial Adhesives, Inc. This adhesive is a two-part system designated IA-125 and IA-804. IA-125 is the basic resin which consists of an approximately 5% solution of a hydrox-terminated, unsaturated polyester in methyl ethyl ketone. The curing agent, IA-804, is an approximately 5% solution of a diisocyanate in methyl ethyl ketone.

For some later studies epoxy resins were employed. Mixtures of EPON 828 with a "flexiblizer" resin, EPON 871, were cured with EPON curing agent Z. A wide range of resin properties from very stiff and brittle (828/871 ratio of 75/25) to quite flexible (828/871 ratio of 25/75) could be achieved with this system. With this system fiber pen tips were produced with essentially no voids between filaments for ink flow.

B. Fabrication Procedures

Rod stock was prepared using the mold shown in Figure 1. Two different fabrication procedures were used. Fiber under controlled tension (G.E. Hysteresis Brake) was dipped in resin, partially dried, and passed through the mold heated to 450°F. Careful control of the residual solvent content was

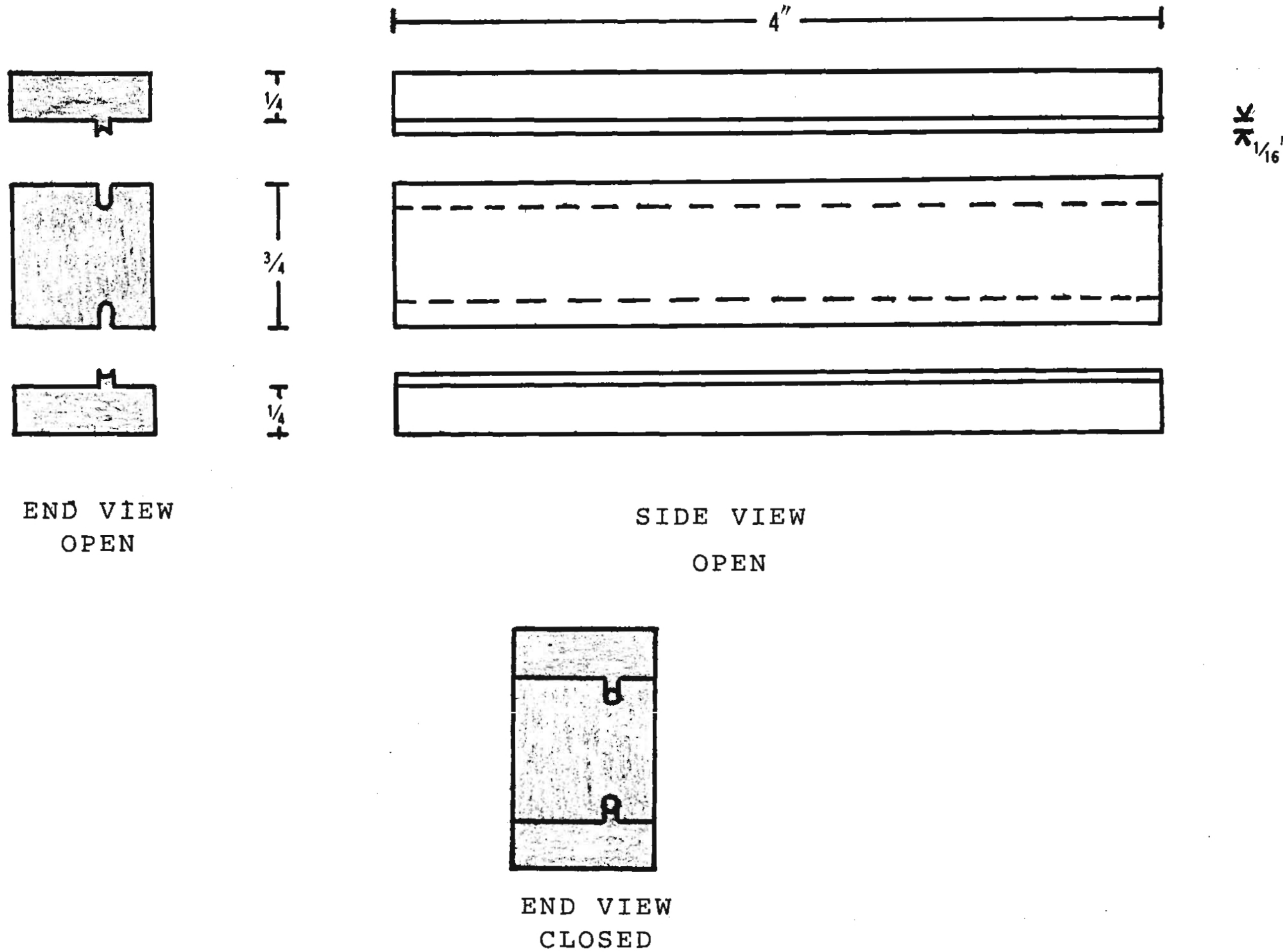


Fig.1-- Drawing of Die Used For Rod Stock Production

necessary to achieve good adhesion between filaments. The second procedure involved impregnation of the yarn with resin and winding on the mold. The resin was then cured by placing in a heated oven for the recommended cure cycle. This second procedure was used exclusively with the epoxy resins.

4. Pen Tip Evaluation

A number of procedures were used for pen tip evaluation. In early experiments the rate at which two Scripto inks (Red-3806B and Black-3886) rose in the pen tips by capillary action was determined and compared with standard Scripto pen tips. It became apparent after a number of experiments that this technique was not a good measure of the ability of the tip to deliver ink to a writing surface. Very rapid rise rates were observed in some tips but sufficient volumes of ink were not transported to achieve good writing characteristics

Microscopic examination was used in an attempt to better evaluate the characteristics of various pen tips Sections of tips were cut from rod stock, placed on the stage of a standard microscope and examined by reflected light. Resin distribution, mechanism of ink transport and quantity of ink at the surface of the tip could be assessed in this way.

Finally, crude pen tips were constructed from some samples and used in simple writing experiments. No samples performed sufficiently well in these experiments to justify full evaluation on a writing machine.

C. Results

1. Antron II Hollow Filament Pen Tips

Rod stock was prepared from Antron II hollow filament yarns containing 11, 12, and 13 strands of 80 filament, 15 denier-per-filament yarn (880, 960, and 1040 total filaments in the 3 samples). Yarn was dipped in resin (IC-125 and IC-804), dried, and cured in the heated dye similar to the process currently used by Scripto. Approximately 30% by weight resin was added and samples were cured at 450^{o}F. It became apparent in these early experiments that the control of residual solvent present in the resin as it entered the dye was critical to good pen tip properties. If too much methyl ethyl ketone was present, pen tips with resin poor centers were produced. Too little solvent yielded tips that had almost no adhesion between filaments. Apparently, some residual solvent was necessary to allow the resin to flow and properly adhere to the fiber during passage through the die. The solvent evaporation process is further complicated by the fact that chemical reactions between the isocyanate and polyester components of the resin occur during solvent removal.

Control of the residual solvent content at the point at which the fiber enters the dye is extremely difficult as the resin system, as supplied, contains 95% methyl ethyl ketone. A large volume of solvent must therefore be removed at a carefully controlled rate and to a carefully controlled level. These requirements create great difficulty in both laboratory and commercial production of rod stock.

Times for ink to rise 3/4" in each of the three pen tips were determined and are given in Table I. The results shown are averages of 5 different runs. Data from three commercial pen tips -- Dorex III, Anja (Regular), and Anja (A.V.) -- are also shown. The samples produced from hollow fibers appear to have rise rates similar to the Dorex III tips in both red and black ink but much shorter rise rates than the Anja tips with black ink.

Perhaps the most significant conclusion from these data is that the rate of rise decreased with increasing numbers of filaments in the tip. This suggests that the ink was being transported in spaces between filaments rather than through the hollow channels in the filaments.

TABLE 1

TIME FOR INK TO RISE 3/4" IN PEN TIPS

	RED INK #3806B (SEC.)	BLACK INK #3886 (SEC.)
DOREX III.	24.5	17.0
ANJA (REGULAR)	38.3	>100
ANJA (A.V.)	34.6	>100
11 STRANDS ANTRON II	12.8	21.4*
12 STRANDS ANTRON II	54.5	23.7*
13 STRANDS ANTRON II	69.5	26.2*

*The black ink was transported almost exclusively by the interior portion of the rod stock rendering observation of ink rise very difficult.

Microscopic investigation of the pen tips revealed that this was the case. When a tip containing hollow filaments was brought in contact with ink on the microscope stage, the channels within the hollow filaments fill very rapidly with ink. This very rapid wicking of ink in fiber channels is very difficult to see in the fabricated tip with the unaided eye. Ink could also be observed filling the voids between filaments at a much slower rate. This latter process was the one observed and recorded in Table 1. Since the ink was rising in the tips by a similar process in both the hollow fiber and the commercial tips, it is not surprizing that similar rise rates were observed.

Resin "poor" central regions were observed under the microscope for some pen tips fabricated from hollow filament yarns. These regions were undoubtedly produced by too rapid removal of the resin solvent.

Crude pens fabricated from the 11, 12, and 13 strand Antron II fiber were prepared and tested. Acceptable quantities of ink were delivered by these tips to the writing surface. Microscopic studies, however, indicated that the major portions of the ink was being carried by spaces between filaments.

In order to properly evaluate the hollow filament pen tips, it was necessary to prepare tips in which all spaces between filaments were completely filled with resin. All ink flow could then be attributed to transportation of ink by the hollow filaments. Repeated attempts to prepare rod stock with spaces between filaments filled with resin were made with the Scripto resin system. This was not possible even with a 50% reduction in solvent content prior to application of resin to the fiber. Subsequent experiments were therefore conducted with an epoxy resin system.

A number of pen tips were prepared containing Antron II hollow filaments in a variety of epoxy resins. These tips had fiber loadings similar to those listed in Table 1 and microscopic investigation revealed that all spaces between filaments were completely filled with the resin system. It was further observed that ink readily flowed through the channels in the fibers but it was apparent that sufficient volumes were not delivered for an acceptable writing instrument. Attention was therefore directed to both very small and very large hollow filaments to determine if sufficient ink flow could be achieved.

2. Studies on Large and Small Diameter Hollow Filaments.

Two samples of fibers used in reverse osmosis ultra-filtration units were employed in these studies (see Figure 2). These fibers have a significant cellulose acetate content and could not be fabricated with the Scripto resin system containing 95% methyl ethyl ketone. All studies with these hollow filaments were made on rod stock fabricated with Epoxy resin systems. These rods were examined under the microscope to ensure that all ink flow was occurring within the interior of the hollow filaments. Crude pen tips were fabricated and tested, but neither tip was capable of delivering a sufficient volume of ink.

A significant difference was observed in the ink delivery capacity of the large and small hollow tips. The small fibers with large numbers of ink carrying channels were capable of delivering a larger volume of ink to a writing surface.

3. Studies on Resin Systems

Although not a specific objective of the present effort, several different resin formulations were used in the studies described above. The resin system had a significant effect on the delivery of ink to the writing surface, even in those cases in which ink transport occurred within hollow filaments. The

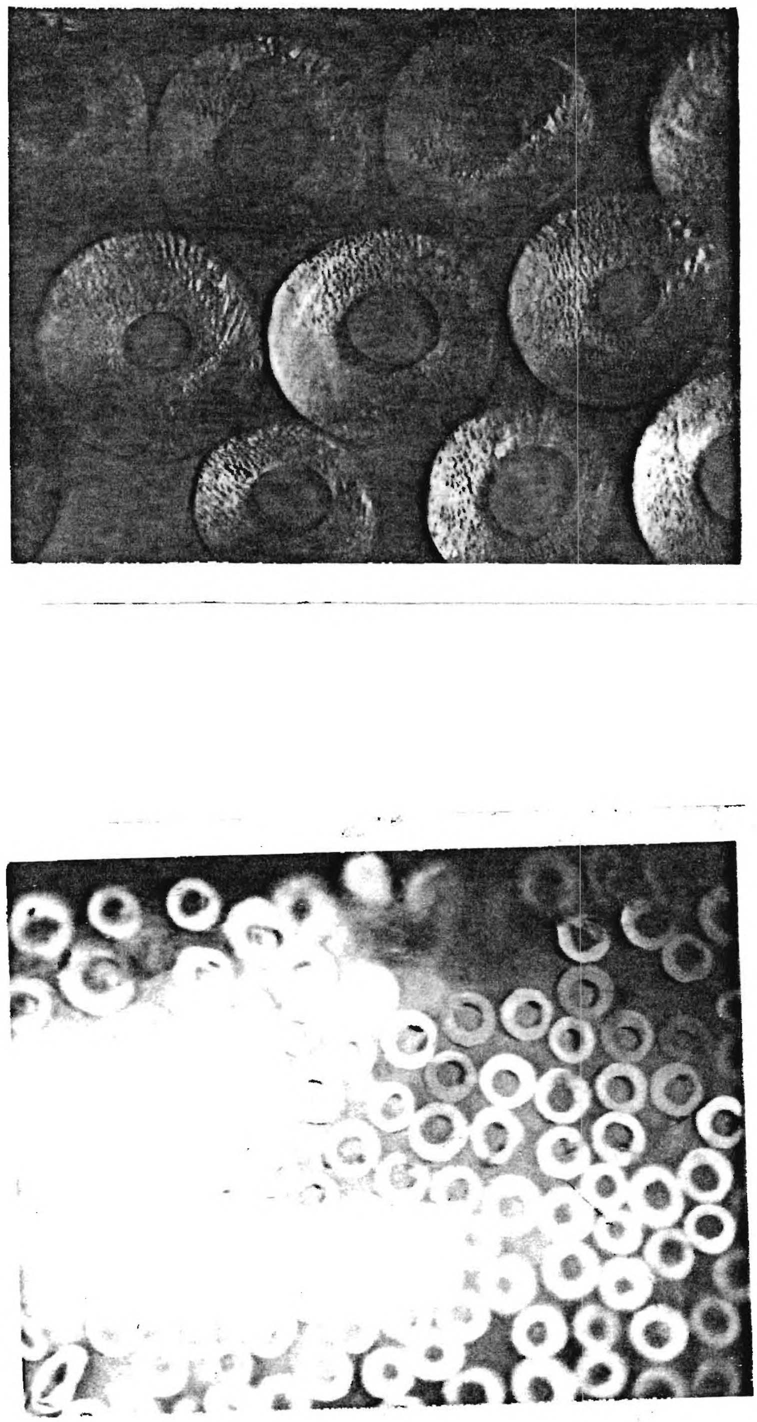


Figure 2 - Large and small hollow filaments used for porous pen tips.

transfer of ink from the tip to a writing surface is strongly dependent on the mechanical properties of the resin. Very stiff resins allowed only a small area of contact between tip and paper, whereas more flexible resins permitted large areas to be in contact. Ink transfer was, of course, closely related to the area of contact.

D. Conclusions and Recommendations

1. The results of these experiments suggest that hollow filaments offer no significant advantages over other types of fibers for fiber tip pens. In no case in which all ink transport was occurring within hollow filaments could sufficient ink be delivered to the writing surface. Observations of many pen tips under the microscope suggest that one reason for this may be that channels in hollow filaments are completely isolated from each other. Only those channels in direct contact with the writing surface are transporting ink at any instant in time. In other porous fiber composites with random voids, many different and interconnecting pathways are available from the ink supply to the pen tip. This interconnection between channels could account for the ability of random porous composites to deliver large quantities of ink, even when only a small portion of the tip is in contact with a writing surface.

2. The major problem in control of the Scripto manufacturing process appears to be inherent in the resin system employed. Control of the rate of evaporation of large volumes of solvent, control of the quantity of residual solvent, and control of the chemical reactions involved with resin curing at one and the same time seems highly impractical. A resin system in which solvent evaporation (if essential), prepolymer formation and curing can be separately controlled (e.g. Epoxy based systems) would be highly desirable. Changes in the resin system are believed to be essential to improved control of the Scripto process.

3. A structured cross-section fiber should provide a better system for introducing controlled void space between filaments. These fibers are commercially produced in star, triangular, trilobal, and triskellian shapes. These fibers pack much less efficiently than round cross-section fibers and are available in a number of sizes and yarn configurations.
4. Further research work on process control should be directed toward improvements in the resin system. The resin must be extremely tough and have a high flexibility with a controlled degree of porosity. One very promising approach would be to use a mixture of low melting point and high melting point fibers and to pass the blend into a die heated to a temperature sufficient to melt the lower melting component. This component, on cooling, could then serve to bond the remaining filaments at fiber-fiber crossing points. A second approach would be the use of a two-stage curing epoxy resin system. This system should permit fabrication of rod stock by passing precoated yarns into a heated die.
5. A "sheath-core" pen tip may also have merit. The central fibers in the tip are subjected to most of the mechanical action during writing. It should be possible to apply one resin system selected for good mechanical properties to approximately 25% of the fibers and to apply a second resin system selected for high porosity to the other 75%. In fabrication of the tip, the fibers with the superior mechanical properties could be assembled in the central region of the pen tip by techniques similar to those employed in sheath-core spinning of bicomponent yarn structures. A tip constructed in this way should combine both of the critical properties required for good fiber tip pens in an easily controlled process.

E-27-619

MELT BONDED BICOMPONENT

FIBER TIP PENS

Final Report
Project E-27-619
Phase II

For

Scripto, Inc.

February 10, 1975

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SUMMARY

This project was undertaken to evaluate possible modifications to the Scripto process for manufacture of fiber tip pens to improve control of pen quality. Acceptable pens must combine resistance to tip breakdown with sufficiently high porosity to deliver the quantity of ink necessary for writing.

Emphasis in the initial phase of study (Ref. 1) was directed to evaluation of hollow fibers as a means for incorporating controlled porosity with acceptable mechanical properties. During the course of these studies it became apparent that the resin system employed in the Scripto process is the component creating greatest variations in pen tip quality. Studies in Phase II have therefore been directed toward development of an improved bonding system.

Pen tip rod stock was prepared by passing mixtures of Nylon 6 and Nylon 6,6 yarns through a die heated to 220 to 230°C. The Nylon 6 component melted at these temperatures, and on cooling, bonded the Nylon 6,6 fibers together. Control of mechanical properties and porosity was achieved by varying the nylon 6 to nylon 6,6 ratio and by changes in the yarn structure (number of plys and twist level).

Preliminary evaluation of pen tips suggest that melt bonding of bicomponent yarn assemblies shows promise as a simple , easily controlled process for manufacture of rod stock for fiber tip pens. More extensive writing machine experiments will be necessary to fully evaluate this approach.

TABLE OF CONTENTS

I. Introduction

Porous tip pens have captured a significant part of the writing instrument market in the past several years. Two principal approaches have been taken in manufacture of tips for these pens. One process involves use of either adhesive or thermal bonding to bind a bundle or mat of fibers in such a way that channels for ink flow are present between filaments. In the second process, spheres of a suitable plastic material are fused together by heat and pressure to form a porous pen tip. There are advantages and disadvantages to both of these approaches.

Scripto, Inc. has previously produced fiber pen tips by dipping a textured Nylon 6,6 fiber in a resin system and curing the resin to give controlled cementing of the filaments so that a porous pen tip is produced. This pen tip has excellent properties but significant difficulties were encountered in controlling the process to consistently yield high quality pen tips. The evaporation of a large volume of solvent (95% of the resin system) at a controlled rate and to a precise residual level is extremely difficult to achieve in both laboratory and commercial processes. Development of a new fiber bonding system appeared essential to establishing a controlled manufacturing process for fiber pen tips.

II. Objective

The objective of the research project was to evaluate modification of the present process for improved control of pen quality. The second phase of the project has been directed toward development of a new more easily controlled bonding technique (melt-bonding) for production of fiber pen tips.

III. Conclusions

Pen tips were prepared with varying quantities and ratios of nylon 6 to nylon 6,6 from 2:1 to 1:4 with both twisted and plyed and untwisted yarns. Samples were bonded by passing the fiber assembly through a die heated above the melting point (218°C) of the Nylon 6 component. Tips were evaluated by measuring rate of rise of ink in tips, by inspection under the microscope, and by preparing simple tips for writing experiments. These studies suggest that:

1. The mechanical properties of melt-bonded pen tips are directly proportional to the quantity of Nylon 6 in the tip. The porosity and therefore the ink transport capacity is inversely proportional to the Nylon 6 ratio.

2. At a given nylon 6 to nylon 6,6 ratio, mechanical properties improved with a higher number of nylon 6,6 filaments but porosity decreased.

3. Tips from fiber assemblies prepared from twisted and plied yarns gave more uniform pen tips.

4. Melt-bonding of bicomponent fiber assemblies shows promise as a simple, easily controlled process for manufacture of tips for fiber pens.

IV. Recommendations

Preliminary evaluation of pen tips prepared by melt-bonding suggests that this technique should be investigated in greater detail. In particular, extensive writing machine evaluation of pen tip candidates will be required for further development of the process. It is estimated that approximately 6 months effort at a cost of $8,500 would be required to develop a commercial process based on the melt-bonding approach.

V. Technical Details

A. Problem Definition

Scripto has produced pen tips from a multi-filament, Nylon 6,6 stretch yarn impregnated with a polyester resin and cured with an isocyanate. Yarns from a creel under controlled tension were dipped in a 5% solution of the adhesive in methyl ethyl ketone. Most of the solvent was removed by evaporation and the yarn passed into a heated die. The adhesive was partially cured in the die and the cure cycle completed in a post cure oven. Pen tips were then cut and shaped in a grinding operation.

Tips produced by this process have good properties but control of the process presented a number of problems. First, nylon stretch yarn undergoes significant changes in dimensions with only small changes in tension. It was necessary therefore to carefully control tension of the yarn during the process. Second, the various stages involved in a conversation of the liquid adhesive system to a solid polymer (i.e., evaporation of solvent, reaction of isocyanate groups, crosslinking) could not be independently controlled. These control problems manifest themselves either as tips with an excess of resin resulting in poor ink flow, or tips with a deficiency and/or improper distribution of resin resulting in poor mechanical properties.

In the latter case, early destruction of the adhesion between filaments gives a splaying of the tip and a very wide writing line.

The present research effort was undertaken to develop a simple, easily controlled process for bonding filaments in a porous fiber assembly for use in pen tips. Since melt-bonding should provide a very easily controlled process, this approach was selected for study. Nylon fibers of two different chemical structures nylon 6 and nylon 6,6, are readily available in a wide range of filament sizes. Nylon 6 melts at approximately 218°C and nylon 6,6 at 256°C. A blend of these two fibers could therefore be passed through a die at a temperature sufficient to melt the nylon 6 component without melting the nylon 6,6. The molten nylon 6 on cooling and solidifying could then serve as the bonding agent between the nylon 6,6 fibers in the pen tip. The availability of materials, the ease of preparation and handling of fiber assemblies and the wide difference in melting points between the two components suggested that this would be a simple system to set up and control.

B. Experimental

1. Materials - Fiber

The nylon 6,6 yarn used in this study was a 143 denier, 71 filament highly textured yarn prepared by Madison Throwing Company. This yarn is identical to the yarn used in Scripto pen tips. The nylon 6 component was a 70 denier 32 filament textured Caprolan yarn produced by Allied

Chemical Company. Melting points of the two fibers are given below:

Fiber	Melting Range
Nylon 6,6	252-254°C
Nylon 6	215-218°C

2. Equipment & Rod Stock Preparation

The various yarn assemblies used in this investigation were prepared on a Whiten Model B Novelty Twister. This machine has the capability of combining up to 12 different yarns into a single yarn assembly. Yarns can be fed into the combined yarn assembly at 2 different speeds and the total twist of the final assembly can be controlled.

In this investigation the nylon 6 and nylon 6,6 were fed into the twister at the same speed. The ratio of nylon 6 to nylon 6,6 was controlled by the number of ends of each yarn in the assembly. For example, a 1:1 ratio was achieved by twisting 2 ends of the nylon 6 (140 total denier) and 1 end of the nylon 6,6 (143 total denier). The combined yarns were given approximately 13 to 17 turns per inch of twist.

In some cases untwisted samples were prepared by combining the appropriate number of nylon 6 and nylon 6,6 yarns with zero twist. The yarn assembly was characterized by the ratio of nylon 6 to nylon 6,6, the number of strands of the nylon 6,6 in the assembly, and whether or not the component yarns had been twisted or were not twisted.

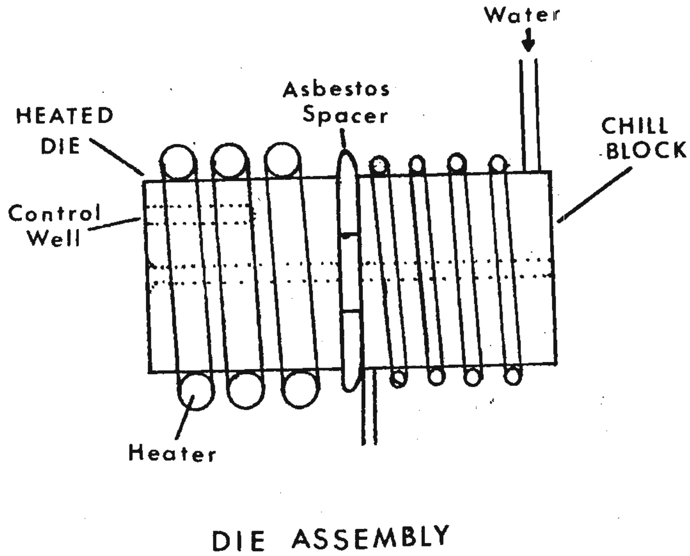
Early rod stock samples were prepared by winding the yarn assembly in a mold and placing the mold in a heated oven to melt the nylon 6 components. This technique did not prove satisfactory because the long times required for heating the yarns to 220°C resulted in considerable degradation of the nylon. A small "bench top" unit was therefore constracted to prepare rod stock samples.

The unit for rod stock preparation is shown in Figure 1. The yarn assembly was prepared by winding the appropriate number of yarns (either twisted or untwisted) on a laboratory skein winder. The unit was prepared by heating the mold to 218-237°C and threading the unit up with flexible woven wire. The woven wire was attached to the yarn assembly and the yarn pulled through the heated die at a rate of 1"/minute. This gives approximately 1 minute residence time in the heated zone. The yarn assembly passed from the heated zone through a chill block to solidify the molten nylon 6. With this unit approximately 18" lengths of rod stock could be prepared.

3. Pen Tip Evaluation

The ability of pen tip stock to transport ink was evaluated by the following procedure. Two inch lengths of rod stock were stapled to rectangular (~2 square inch folded) pieces of filter paper. The end of the rod stock was placed just below the surface of a pool and ink transferred to the paper noted. In some cases the entire filter paper was completely saturated with ink after 10 minutes. In other cases the ink did not rise the 2 inches to the paper in the same time. This test, therefore, gave a good indication of the relative porosities of various rod stock samples.

Promising samples of rod stock were also evaluated by constructing crude pen tips, inserting them into Scripto ink reservoirs and conducting



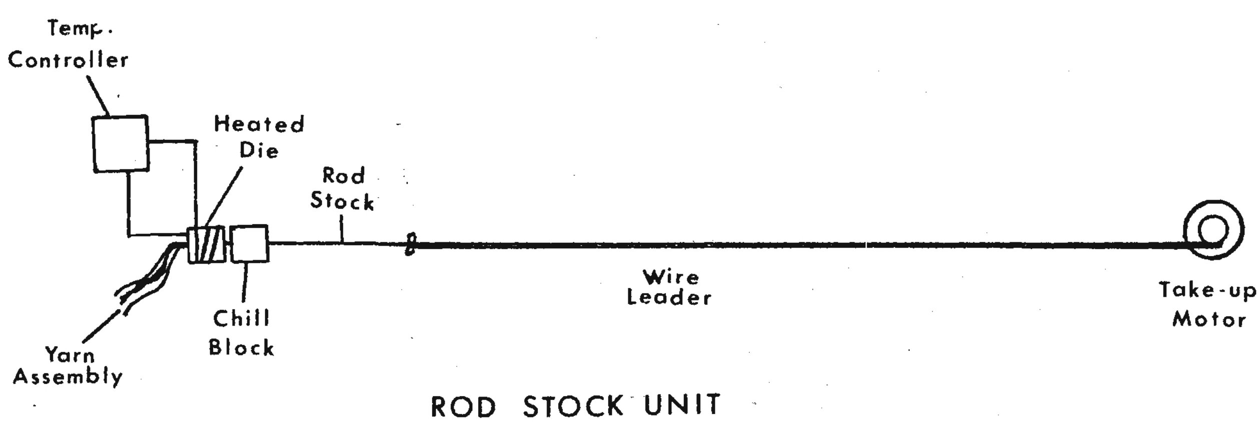


Figure 1. Bench Unit for Production of Rod Stock

writing experiments. Several samples performed well in these crude writing experiments.

C. Results

The samples prepared on the "bench scale" unit are shown in Table 1. The results of studies on ink transport and a subjective assessment of the durability of tips are given in Table 2 for tips prepared from untwisted yarns and in Table 3 for twisted yarn assemblies. The word "dry" in Tables 2 and 3 indicate tips which would not readily transport ink from the reservoir to the paper tab. "Good" is used to describe tips which readily transported ink. "Weak" designates tips with obvious deficiencies in physical properties. Tips with no descriptive terms were so weak as to be of no further interest.

Visual comparison of per tips following ink transport studies clearly indicated that tips prepared from twisted yarn samples showed greater uniformity than those prepared from untwisted yarns. The samples prepared from untwisted yarns had large regions that were totally fused and other areas with regions with little bonding. Subsequent evaluations were therefore limited to twisted yarn samples.

Comparison of the results shown in Tables 2 and 3 show clear differences in physical properties and in ink transport capabilities. Increasing the nylon 6 to nylon 6,6 ratio greatly reduced the rate of ink transport and increases the "hardness" of the tip. The number of nylon 6,6 yarns in the bundle also significantly alters the properties.

TABLE 1

Sample Number	No. of Yarns Nylon 6,6 143/71	No. of Yarns Nylon 6 70/32	Nylon 6 to Nylon 6,6 Ratio	Twist	Speed (In/min)	Temp. °C
110-001-1	56	56	1:2	0	1	218-237
110-001-2	60	60	1:2	0	1	218-237
110-002-1	50	100	1:1	0	1	218-237
110-002-2	56	112	1:1	0	1	218-237
110-002-3	60	40	1:3	0	1	218-237
110-002-4	54	36	1:3	0	1	218-237
110-002-5	48	32	1:3	0	1	218-237
110-002-6	50	50	1:2	0	1	218-237
110-003-1	50	50	1:2	~13 (1:1)	1	218-237
110-003-2	56	56	1:2	~13 (1:1)	1	218-237
110-003-3	60	60	1:2	~13 (1:1)	1	218-237
110-003-4	50	25	1:4	~13 (2:1)	1	218-237
110-003-5	80	40	1:4	~13 (2:1)	1	218-237
110-003-6	76	38	1:4	~13 (2:1)	1	218-237
110-003-7	60	30	1:4	~13 (2:1)	1	218-237
110-003-8	56	28	1:4	~13 (2:1)	1	218-237
110-004-1	69	46	1:3	~13 (3:2)	1	218-237
110-004-2	60	40	1:3	~13 (3:2)	1	218-237
110-004-3	54	36	1:3	~13 (3:2)	1	218-237
110-004-4	51	34	1:3	~13 (3:2)	1	218-237
110-005-1	66	44	1:3	~13 (3:2)	1	218-237
110-005-2	63	42	1:3	~13 (3:2)	1	218-237
110-005-3	57	38	1:3	~13 (3:2)	1	218-237
110-005-4	60	40	1:3	0	1	218-237

TABLE 2

Pen Tips Prepared From Untwisted Yarns

Ration of Nylon 6 to Nylon 6,6

No. of Nylon 6,6 Yarns (143/71)	1:1	1:2	1:3
48			
50	110-002-1 Dry	110-002-6 Good	
54			110-002-4 Good
56	110-002 Dry	110-001-1 Good	
60		110-001-2 Slightly Dry	110-002-3 110-005-4 Good

TABLE 3

Pen Tips Prepared from Twisted Yarns

Ratio of Nylon 6 to Nylon 6,6

Number of Nylon 6,6 Yarns	1:2	1:3	1:4
50 51	110-003-1 Slightly Dry	110-004-4	110-003-4
54		110-004-3 Good	
56 57	110-003-2 Dry	110-005-3 Good	110-003-8
60	110-003-3 Dry	110-004-2 Good	110-003-7 Good Weak
63		110-005-2 Dry	
66		110-005-1 Dry	
69		110-004-1 Dry	
76 80			110-003-5 110-003-6 Dry

The results suggest two regions which may produce good pen tips. Tips with 50 to 55 ends of nylon 6,6 and a 6 to 6,6 ratio of 1:2 appear to have promising properties. Also, samples with 55 to 60 ends of nylon 6,6 and a 6 to 6,6 ratio of 1:3 should be investigated further.

A number of crude writing experiments were conducted with the more promising pen tip candidates. Short lengths of rod stock (~1") were sharpened with a razar blade, placed in a plastic collar and inserted in an ink filler tube filled with Scripto Black Ink #3886. A number of pen tips constructed in this way from rod stock samples with 6 to 6,6 ratios of 1:3 or 1:2 and 50 to 60 ends of nylon 6,6 produced acceptable pen tips in this crude test.

One interesting observation noted during the writing experiments was that the pen tips became softer after exposure for a few hours to the ink solution. This may indicate that the ink formulation is slightly corrosive to the nylon fiber. This did not appear to be a major problem, however.

Further evaluation of pen tip candidates was not carried out. Testing on writing machines will be required to clearly differentiate samples with varying ratios of 6 to 6,6 and varying numbers of ends of Nylon 6,6 which were found to be good candidates in this study.

D. Conclusions

This study has indicated that pen tips with reasonable properties can be prepared by fusion of yarn assemblies containing mixtures of nylon 6 and nylon 6,6. The porosity and mechanical properties can be varied by either changing the ratio of Nylon 6 to Nylon 6,6 or by changing the total number of nylon 6,6 yarns in the assembly. The process can be easily controlled and should be readily adaptable to production of pen tips.

Further development work will require extensive writing machine evaluation of pen tip candidates to determine the best possible yarn assembly for pen tip production.

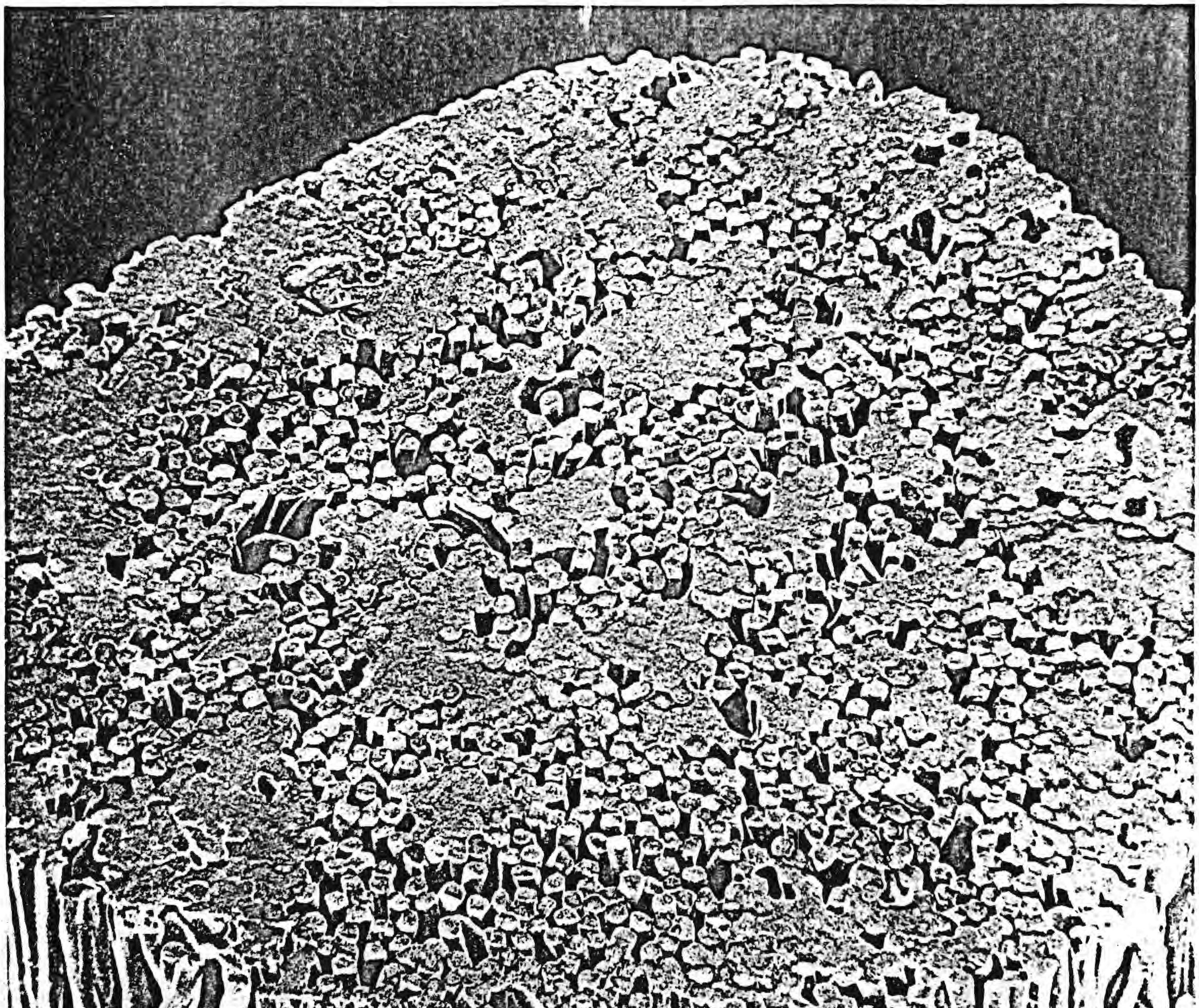
VI. Microscopic Investigation

In one final experiment a sample of Rod Stock Number 017-075-004 was submitted for investigation by scanning electron microscopy. This sample had 54 ends of nylon 6,6 and a ratio of nylon 6 to nylon 6,6 of 1:2 with the two yarns twisted together prior to preparation of the yarn assembly for rod stock formation. A cross-section of this sample is shown in Figure 2.

It is clear from this photograph that bonded areas are uniformly distributed throughout the pen tips. The bonded areas are interspaced with non-bonded regions which should provide good ink transport. Filaments which are not directly bonded in this cross-sectional plane are probably bonded at other points in the tip (and vice versa) as the yarns intermingle and migrate in traversing the length of the pen tip. Figure 2 suggests that the melt bonding approach produces a structure which should have very desirable properties for fiber pen tip production.

VII. References

1. Tincher, W.C.: "Porous Composites for Fiber Tip Pens". Final Report - Project E-27-619; Georgia Institute of Technology, March, 1974.



GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ANALYTICAL INSTRUMENTATION LABS

SAMPLE 017-075-004

FIGURE 2.

1μ x100

PROJECT NO. A232-734 MAGNIFICATION 110X

SAMPLE NO. Exp.Pt.-Sm-1-B(x sec) DATE 2-13-75